



ENGINEERING SERVICE CENTERPort Hueneme, California 93043-4370

CONTRACT REPORT CR 05-006-ENV

LONG TERM PERFORMANCE ASSESSMENT OF A PERMEABLE REACTIVE BARRRIER AT FORMER NAVAL AITR STATION MOFFETT FIELD

by

A. Gavaskar

W. S. Yoon

J. Sminchak

B. Sass

N. Gupta

J. Hicks

V. Lal

July 2005

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0811

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information, it if does not display a currently valid OMB control number.

			04, Arlington, VA 22202-430 ction of information, it if does			e aware that notwithstanding any other provision of law, no person d OMB control number.
PLEASE DO	NOT RETURN Y	OUR FORM TO	THE ABOVE ADDRE	ESS.		
	TE (DD-MM-YYYY)		2. REPORT TYPE			3. DATES COVERED (From - To)
July 2005			Final			
4. TITLE AND S					5a. (CONTRACT NUMBER
	_		ESSMENT OF A			
			AT FORMER NA	AVAL AIR	5b. (GRANT NUMBER
STATION	MOFFETT F	IELD			F	PROGRAM ELEMENT NUMBER
					5C. F	PROGRAM ELEMENT NUMBER
AUTUOR(O)						DDO JEST NUMBER
6. AUTHOR(S) A Gavaska	r. W. S. Yoon.	I Sminchak F	3. Sass; N. Gupta; J	Hicks:	5ú. i	PROJECT NUMBER
and V. Lal	a, ,, ,, b. 1 0011,	v. Siiiiiviiak, E	. 5 4 55, 11. Gupta, v	. 1110115,	5e. 1	TASK NUMBER
wire v. Eur						
					5f. V	VORK UNIT NUMBER
7. PERFORMIN	G ORGANIZATION NA	ME(S) AND ADDRES	SES			8. PERFORMING ORGANIZATION REPORT NUMBER
Commandi						
	lities Engineerii	ng Service Cen	ter			CR-05-006-ENV
1100 23 rd A						
Port Huene	me, CA 93043-	•				
a sponsopin	G/MONITORING AGEN	ICV NAME(C) AND A	DDDECC/EC)			10. SPONSOR/MONITORS ACRONYM(S)
			ification Program			ESTCP
	Stuart Street, Su		inoution i rogium			ESTCI
Arlington,						11. SPONSOR/MONITOR'S REPORT NUMBER(S)
811,						
12. DISTRIBUTI	ON/AVAILABILITY ST	ATEMENT				
		4				
Approved f	for public releas	se; distribution	is unlimited.			
13. SUPPLEME	NTARY NOTES					
14. ABSTRACT						
The prin	nary objective o	of this report is	to describe the resu	ılts of the last	rour	nd of monitoring conducted in July 2004,
their relation	onship to the res	ults of perviou	s rounds, and their	implications t	for th	ne longevity and hydraulic performance of
the permea	ble reactive bar	rier (PRB).				
15. SUBJECT T	EDMS					
	reactive barrier	(PRB), Enviro	nmental Security T	echnology Co	ertific	cation Program (ESTCP), zero valent iron
(ZVI)						
	CLASSIFICATION OF:		17. LIMITATION OF	18. NUMBER OF	=	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	ABSTRACT	PAGES		
IJ	IJ	U	U	37		19b. TELEPHONE NUMBER (include area code)

Long-Term Performance Assessment of a Permeable Reactive Barrier At Former Naval Air Station Moffett Field

Contract No: N47408-01-D-8207 Task Order No: 0091

Prepared for:

N. Ruiz and C. Reeter Project Officers Naval Facilities Engineering Service Center Port Hueneme, California

Project sponsored by:



Prepared by:

A. Gavaskar, W.S. Yoon, J. Sminchak, B. Sass, N. Gupta, J. Hicks, and V. Lal Battelle 505 King Avenue Columbus, Ohio 43201

June 24, 2005

ACKNOWLEDGEMENTS

This study was funded by the Department of Defense's (DoD) Environmental Security Technologies Certification Program (ESTCP) through the Naval Facilities Engineering Service Center (NFESC). Battelle, under contract to NFESC conducted the laboratory and field investigation associated with the study. The authors also acknowledge the support provided by Mary Parker from Navy's Southern Division and by several staff from Tetra-Tech EMI, the on-site Navy contractor, who provided additional field support.

EXECUTIVE SUMMARY

A permeable reactive barrier (PRB) filled with zero-valent iron (ZVI) was installed at former Naval Air Station (NAS) Moffett Field in April 1996 and monitored periodically for the next 8 years. This pilot-scale PRB intercepts the more concentrated core of a relatively large regional groundwater plume of CVOCs that is approximately two miles long and a mile wide. The primary objective of this report is to describe the results of the last round of monitoring conducted in July 2004, their relationship to the results of pervious rounds, and their implications for the longevity and hydraulic performance of the PRB.

The primary contaminant in the plume is trichloroethylene (TCE). Considerable amount of *cis*-1,2 dichloroethylene (DCE) is also present in the groundwater, thus indicating that some natural attenuation through anaerobic reductive dechlorination is underway at the site. The cleanup targets for these two compounds are the same as the federal drinking water standards or maximum contaminant levels (MCL) of 5 ppb (TCE) and 70 ppb (DCE).

The long-term monitoring of this PRB showed that the ZVI continues to react strongly with the chlorinated volatile organic compounds (CVOC), primarily TCE and DCE, present in the groundwater. For the first time in July 2004, there were signs that a treated water front was exiting the PRB, flushing portions of the downgradient aquifer, and causing a reduction in CVOC concentrations in the downgradient aquifer. Because of geologic heterogeneity, groundwater flow is faster in the deeper portions of the aquifer, leading to faster flow, less residence time of CVOCs in the reactive cell, and greater mass flux of dissolved inorganic species through the ZVI in the deeper layers. These factors appear to have led to relatively faster aging of the ZVI in the deeper portion of the PRB and less degradation of DCE in the groundwater flowing at that depth. Water level measurements in the wells in and around the PRB showed no noticeable changes in hydraulic capture and flow through the PRB in the 8 years of operation.

This study was funded by the Department of Defense's (DoD) Environmental Security Technologies Certification Program (ESTCP) through the Naval Facilities Engineering Service Center (NFESC). Battelle, under contract to NFESC, planned and conducted the performance assessment activities and prepared this report.

TABLE OF CONTENTS

ACKNO	OWLEDGEMENTS	ii
EXECU	TIVE SUMMARY	iii
FIGUR	ES	iv
TABLE	S	v
Section	1.0: INTRODUCTION	1
Section	1.0. INTRODUCTION	1
Section	2.0: PERFORMANCE ASSESSMENT METHODS	6
Section	3.0: PERFORMANCE ASSESSMENT RESULTS	12
3.1	Trends in TCE	16
3.2	Trends in DCE	16
3.3	Trends in ORP and pH	18
3.4	Trends in Native Geochemical Constituents	21
3.5	Hydrogeologic Trends	24
Section	4.0: CONCLUSIONS	28
Section	5.0: REFERENCES	29
	FIGURES	
	-1. TCE Plume in Groundwater at Moffett Field	
Figure 1	-2. Construction Details of PRB at Former NAS Moffett Field	3
Figure 1	-3. Column Test Results Showing the Increases in TCE Half-Life Due to the Aging of ZVI UExposure to Several Pore Volumes of Groundwater Containing (a) Moderate and (b) High Company (a) Moderate and (b) Moderate	h
г. 1	Levels of TDS	
	-4. Tracer Test Showing Preferential Pathways Through the Iron Medium	
	-1. Illustration of Geologic Setting at Moffett Field	
	-2. Solute Transport Modeling in Different Stratigraphic Layers-3. Location of Model Boundaries and Monitoring Wells in the Vicinity of the Permeable	8
Figure 2	Barrier	0
Eigura 2	-4. Location of Monitoring Wells in and Around the PRB	
	-1. Spatial and Temporal Trends in TCE in Shallow (A and B) and Deep (C and D) Wells	
	-1. Spatial and Temporal Trends in TCE in Shallow (A and B) and Deep (C and D) Wells	
	-2. Spatial and Temporal Trends in TCE in Shallow (A and B) and Deep (C and D) Wells	
	-3. Spatial and Temporal Trends in TCE in Shallow (A and B) and Deep (C and D) Wells	
	-4. Spatial and Temporal Trends in SO ₄ and Alkalinity in and Shallow (A and B) and Deep	
1 15010 3	and D) Wells	
Figure 3	-6. Water Level Maps for A and B Level Wells	
	-7. Water Level Maps for C and D Level Wells	

TABLES

Table 2-1.	Performance Assessment Schedule	6
Table 3-1.	Monitoring Results for Primary Target CVOCs in Groundwater	12
Table 3-2.	Monitoring Results for Field Parameters in Groundwater	13
Table 3-3.	Key Cations in Groundwater	14
Table 3-4.	Key Anions in Groundwater	15
	Vertical Gradients in the PRB	

Section 1.0: INTRODUCTION

A permeable reactive barrier (PRB) filled with granular zero-valent iron (ZVI) (-8+50 mesh, Peerless Metal Powders, Inc. Detroit, Michigan) was installed at former Naval Air Station (NAS) Moffett Field in April 1996 and monitored periodically for the next 8 years, thus providing some understanding of the long-term field performance of PRBs. This pilot-scale PRB intercepts the more concentrated core of a relatively large regional groundwater plume of chlorinated volatile organic compounds (CVOCs) that is approximately two miles long and a mile wide (see Figure 1-1). The primary objective of this report is to describe the results of the last round of monitoring conducted in July 2004, their relationship to the results of pervious rounds, and their implications for the longevity and hydraulic performance of the PRB.

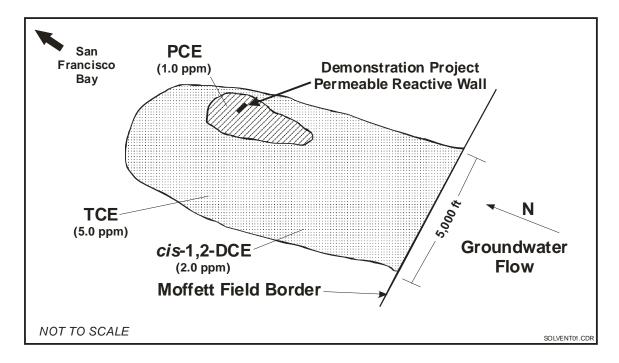


Figure 1-1. TCE Plume in Groundwater at Moffett Field

This study was funded by the Department of Defense's (DoD) Environmental Security Technologies Certification Program (ESTCP) through the Naval Facilities Engineering Service Center (NFESC). Battelle, under contract to NFESC, planned and conducted the performance assessment activities and prepared this report. Reports describing the results of earlier (pre-2004) studies are available on the ESTCP website at www.estcp.org (Gavaskar et al. 1998; Gavaskar et al., 2002).

The primary contaminant in the plume is trichloroethylene (TCE). Considerable amount of *cis*-1,2 dichlorotehylene (DCE) is also present in the groundwater, thus indicating that some natural attenuation through anaerobic reductive dechlorination is underway at the site. The cleanup targets for these two compounds are the same as the federal drinking water standards or maximum contaminant levels (MCL) of 5 ppb (TCE) and 70 ppb (DCE).

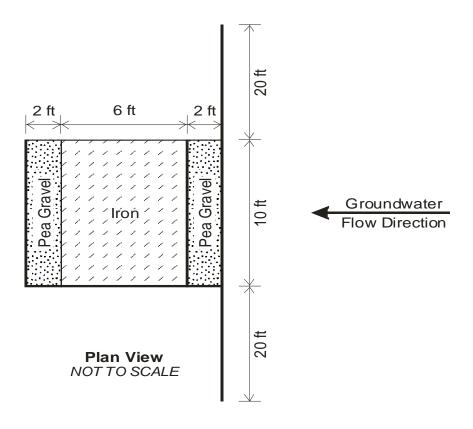
The PRB at Moffett Field is one of the earliest PRBs and is configured as a funnel-and-gate system, consisting of a permeable reactive section (10 ft long) and two impermeable walls (each 20 ft

long and made from interlocked sheet piling) that are expected to enhance groundwater capture and treatment. As shown in Figure 1-2, the permeable section or gate consists of a 6-foot thick (dimension in the direction of flow) reactive cell containing the iron and thinner upgradient and downgradient pea gravel sections. These pea gravel sections, which were popular in the early days of the technology, are expected to facilitate mixing and redistribution of the contamination entering and leaving the PRB, so as to better utilize a limited mass of iron.

The ability of ZVI to degrade CVOCs primarily by relatively fast beta-elimination (abiotic) reactions to ethene and chloride has been described in detail by Roberts et al. (1996). Typically, the more oxidized CVOCs, such as PCE and TCE, react much faster and have much lower half-lives compared with the less oxidized byproducts, DCE and vinyl chloride (VC). DCE and VC are co-contaminants with the parent compounds TCE and PCE at most sites where any degree of microbe-driven natural attenuation is occurring. In addition to the CVOCs, native inorganic parameters (e.g., calcium, magnesium, and alkalinity) are present in the groundwater and react with the ZVI to form precipitates that could potentially deposit on and passivate the ZVI surfaces (Liang et al., 2000). However, these changes typically are expected to take place over several years and this is the reason why the PRB needs to be monitored over the long term.

To supplement the field study, a long-term column study conducted by the authors to estimate the rate of decline in iron performance due to exposure to native inorganic constituents in the groundwater was conducted by the authors in 2001 (Gavaskar et al, 2002). Using groundwater from two PRB sites (Moffett Field and Lowry Air Force Base) the authors showed that the rate of decline in TCE reaction rate (or increase in TCE half-life) is proportional to the level of total dissolved solids (TDS) in the groundwater and the amount of groundwater that the ZVI is exposed to, as shown in Figure 1-3 (Gavaskar et al., 2002). The groundwater from Moffett Field, which contained moderate levels of TDS (500-1,000 mg/L range) showed a more moderate decline in TCE half-life compared to the groundwater from former Lowry Air Force Base, which contained relatively high levels of TDS (greater than 1,000 mg/L). In other words, the aging of the ZVI was proportional to the mass flux of inorganic constituents, such as calcium and carbonates, through the ZVI. One of the objectives of the long-term monitoring of the PRB at Moffett Field was to examine the potential for aging of the iron in a field system and verify the laboratory trends.

Because the hydraulic gradients in the high-porosity high-permeability environment inside the PRB often are relatively flat, water level measurements do not provide sufficient delineation of flow inside the PRB. To supplement the ongoing water level measurements in and around the PRB after installation, a tracer test was conducted in 1997 to examine the flow patterns inside the PRB. Although considerable efforts were made during the construction of the PRB to pack the iron medium uniformly, the tracer test (see Figure 1-4) showed that there are preferential flow paths in the iron medium (Gavaskar et al., 1998). In addition, the tracer test indicated that some of the vertical heterogeneities in flow in the aquifer persist when the groundwater enters the PRB. There was faster flow occurring in the deeper portion of the aquifer and, therefore, in the deeper portion of the PRB as well. One of the objectives of the long-term monitoring of the PRB was to see if these differences in flow would lead to differences in the CVOC degradation efficiency, differences in the aging of the ZVI, and differences in the flushing of CVOCs in the downgradient aquifer at different depths.



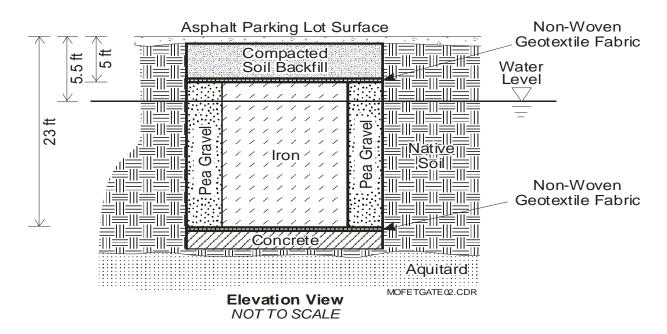
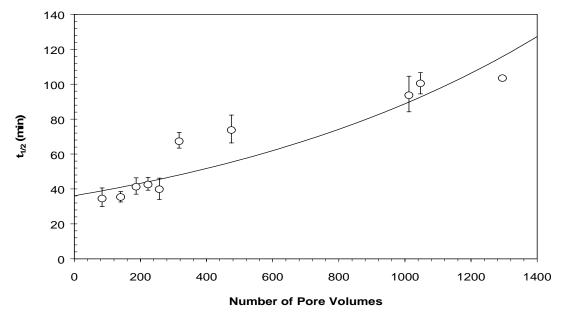
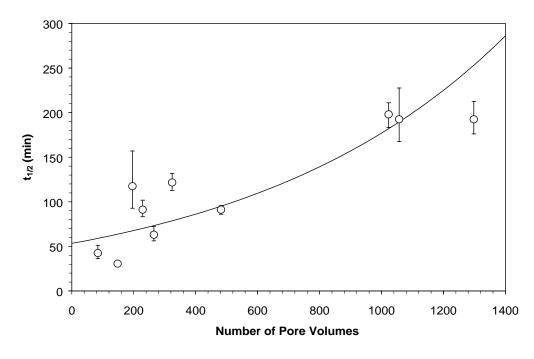


Figure 1-2. Construction Details of PRB at Former NAS Moffett Field



(a) Column simulation of PRB at Moffett Field



(b) Column simulation of PRB at former Lowry Air Force Base

Figure 1-3. Column Test Results Showing the Increases in TCE Half-Life Due to the Aging of ZVI Upon Exposure to Several Pore Volumes of Groundwater Containing (a) Moderate and (b) High Levels of TDS

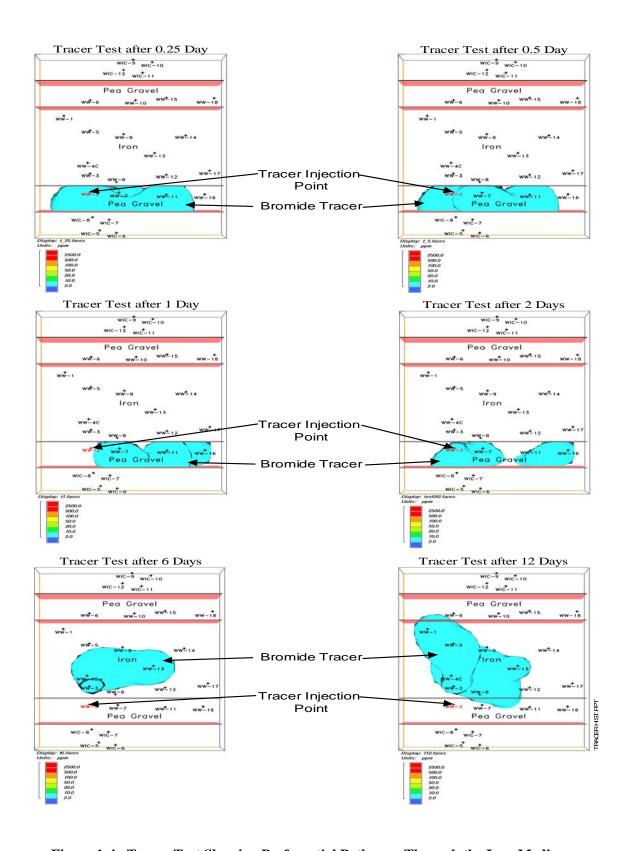


Figure 1-4. Tracer Test Showing Preferential Pathways Through the Iron Medium

Section 2.0: PERFORMANCE ASSESSMENT METHODS

The Moffett Field PRB was monitored from 1996 to 2004. During this 8-year period, several rounds of groundwater monitoring were conducted at this site (see Table 2-1). The layout of the monitoring well network was based on an understanding of the hydrogeology of the aquifer, as determined from cone penetrometer testing (CPT) pushes and groundwater modeling. The conceptual hydrogeologic setting of the PRB is shown in Figure 2-1. Groundwater flow and solute transport modeling (see Figure 2-2) have shown that groundwater (and plume) movement is expected to be much faster in the deeper Layers 3 and 4 than in the shallower Layers 1 and 2 due to the inter-bedded sand and silty clay layers present at the site.

Based on this conceptual model, monitoring wells were installed in and around the PRB at multiple depths along the expected flow path, at the locations shown in Figures 2-3 and 2-4. The wells are arranged in clusters in the upgradient aquifer, upgradient pea gravel, reactive cell (iron), downgradient pea gravel, and downgradient aquifer. Each cluster consists of wells that are designated as A, B, C, and D. The screened intervals of the A and B wells correspond approximately with Layers 1 and 2, which are silty-clay and silt layers, respectively, and contain relatively slower moving groundwater. The B and C wells correspond approximately to the sandy Layer 3 and 4, which contain relatively faster moving groundwater. WIC-1 and WIC-3 are monitoring wells that are further upgradient and downgradient of the PRB and are shown in Figure 2-3. Not all the wells were sampled in all the rounds. Groundwater samples were collected after low-flow purging and analyzed for organic (CVOCs) and inorganic (pH, oxidation-reduction potential [ORP], calcium, magnesium, alkalinity [carbonates], and sulfate) parameters. Water level measurements were collected from all wells.

Table 2-1. Performance Assessment Schedule

Activity	Date Completed
Site characterization	December 1995
Bench-scale tests	October 1995
PRB construction	April 1996
First quarterly monitoring event	June 1996
Second quarterly monitoring event	September 1996
Third quarterly monitoring event	January 1997
Fourth quarterly monitoring event	April 1997
Fifth quarterly monitoring event	October 1997
First tracer test	April 1997
Second tracer test	August 1997
Iron cores collection	December 1997
Final Performance Evaluation Report	November 1999
Groundwater sampling, iron coring	May 2001
Long term column tests	January 2002
Groundwater sampling	July 2004

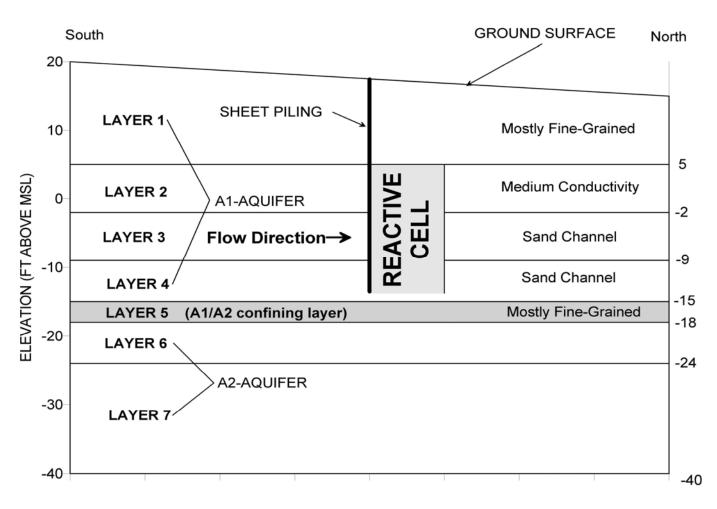


Figure 2-1. Illustration of Geologic Setting at Moffett Field

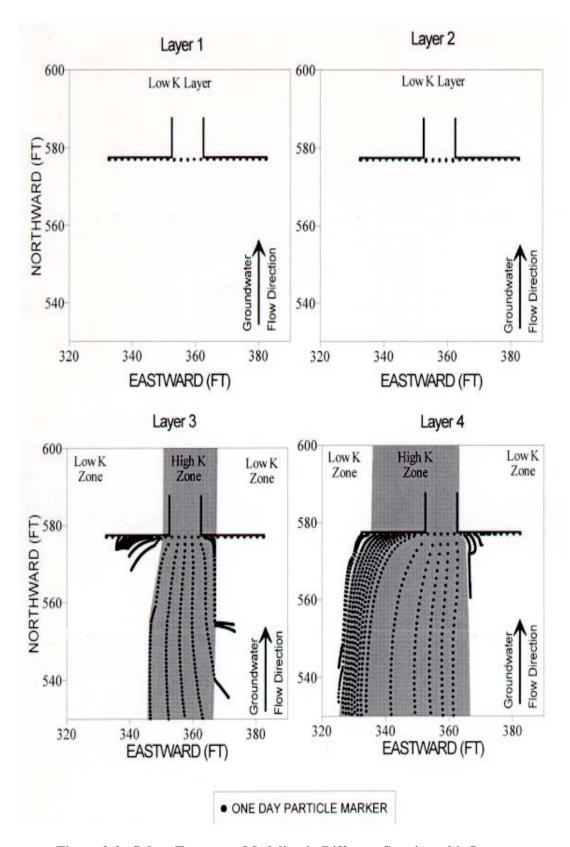


Figure 2-2. Solute Transport Modeling in Different Stratigraphic Layers

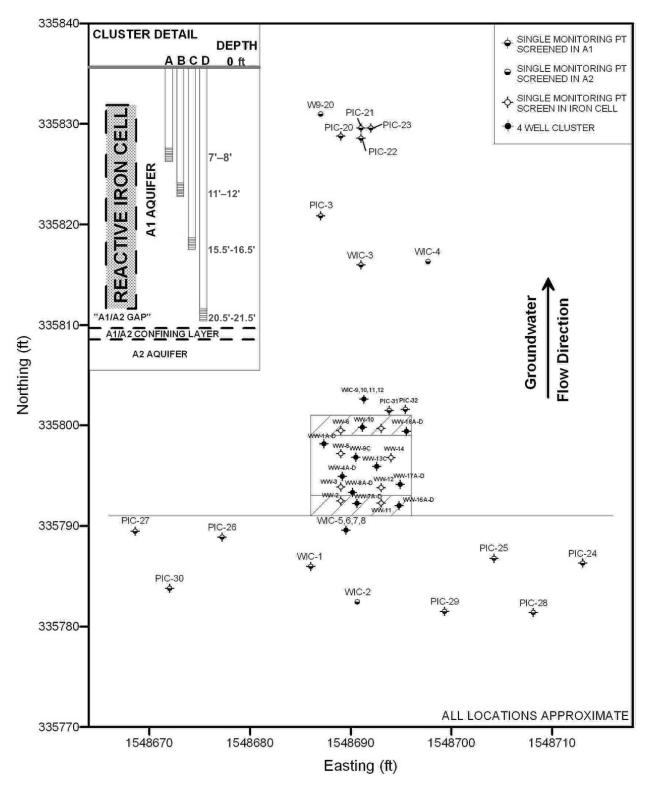
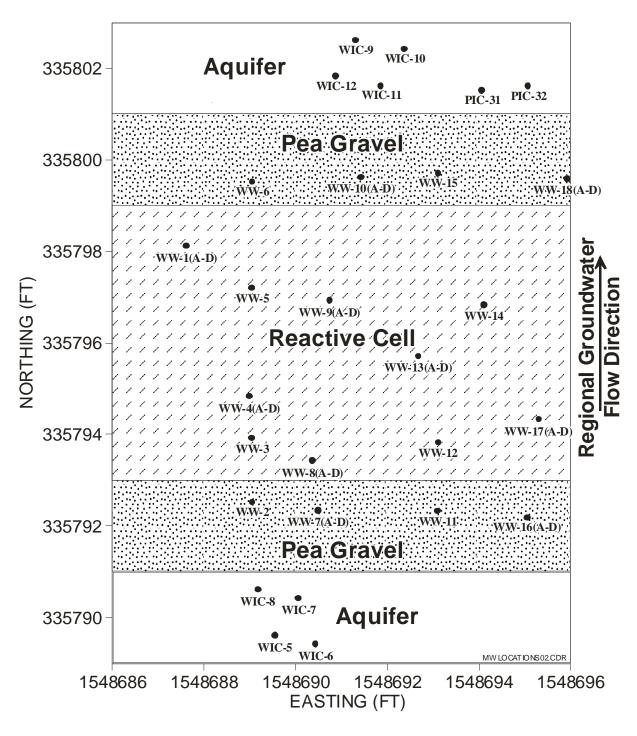


Figure 2-3. Location of Model Boundaries and Monitoring Wells in the Vicinity of the Permeable Barrier



^{*} Easting and Northing coordinates correspond to the California State Plane Coordinate System for zone 403.

Figure 2-4. Location of Monitoring Wells in and Around the PRB

The PRB and all these monitoring wells lie in the shallower aquifer zone (A1), which extends down to 25 ft below ground surface (bgs), and forms part of the surficial aquifer A, which extends down to 60 ft or more. A thin clay confining layer (A1/A2) at 25 ft bgs separates the shallower aquifer zone A1 and the deeper aquifer zone A2. Due to concern over breaching the thin confining layer (A1/A2), the bottom of the PRB was completed a few inches above the confining layer. WIC-8 and WIC-12 are wells in the upgradient and downgradient aquifer, respectively, and are screened at depths close to the confining layer, in order to monitor the effect of this gap.

Quality assurance (QA) for this study included several quality control (QC) checks, including trip blanks, field duplicates, and matrix spikes (MS) and matrix spike duplicates (MSD). The two trip blanks did not show any detected levels of the primary target analyte (TCE). The two pairs of field duplicates showed a precision of 5% and 8% for TCE. Precision was measured as relative percent difference (RPD). MS and MSD recoveries for TCE were 100% and 99.7%, 109% and 102%, and 103% and 104%, respectively, for the three laboratory batches. The laboratory precision, based on the MS/MSD pairs, was 1%, 7%, and 3%, respectively. These QA data indicate that sampling and analysis for this study were conducted in an acceptable manner.

Section 3.0: PERFORMANCE ASSESSMENT RESULTS

Table 3-1 summarizes the results of the CVOC analysis of the groundwater samples collected in select wells along the flow path through the PRB. Table 3-2 contains two important indicator parameters, pH and oxidation-reduction potential (ORP). Tables 3-3 and 3-4 show the results of the analysis of key cations and anions, respectively, in the groundwater. Appendix A contains more detailed monitoring data from the most recent (July 2004) round.

Table 3-1. Monitoring Results for Primary Target CVOCs in Groundwater

	Well ID	Screen		TC	E (ug/L))			DCE (ug/L)			
	Well ID	Depth (ft bgs)	January 1997	April 1997	Oct. 1997	May 2001	July 2004	January 1997	April 1997	Oct. 1997	May 2001	July 2004
	WIC-1	19 – 24	200	2900	NA	1700	NA	230	280	NA	270	NA
Upgradient Aquifer Wells	WIC-5	11 - 12	680	230	180	NA	714	550	340	320	NA	481
Upgradient oquifer Well	WIC-6	15 - 16	1100	1000	1100	NA	905	260	210	250	NA	201
ogra	WIC-7	20.5 - 21.5	960	1200	1300	NA	868	220	190	280	NA	192
U _I	WIC-8	24 - 25	1200	1300	920	NA	827	220	200	170	NA	175
,	WIC-8-DUP		NA	NA	NA	NA	872	NA	NA	NA	NA	184
11	WW-7A	8.08 - 9.08	1800	30	1100	960*	880	300	5	240	230*	198
Up- gradient Pea Gravel	WW-7B	11 - 12.17	1000	1300	1200	960*	819	230	220	250	230*	189
Up- radie: Pea Grave	WW-7C	16 - 17	750	1000	1000	960*	936	210	200	340	230*	203
60	WW-7D	20.67 - 21.33	<2	1700	1600	960*	846	66	240	270	230*	197
	WW-8A	8.25 - 9.42	<20	<2	1	NA	4.55	210	130	200	NA	71.3
	WW-8B	11.08 - 12.08	<10	3	1	NA	2.54	180	120	82	NA	104
	WW-8C	15.92 - 16.75	7	1	.9	NA	3.4	110	49	46	NA	123
	WW-8D	20.5 - 21.5	2	1	.8	NA	0.99	44	42	58	NA	114
	WW-3	10.5 - 20.5	11	3	1.60	2.4*	11.8	220	110	62.52	100*	114
Reactive Wells	WW-4A	7 - 8	<2	<.5	<.5	NA	<2	2	4	<.5	NA	<1
We	WW-4B	10 - 11	<2	<.5	<.5	NA	<2	86	38	6	NA	38
ve	WW-4C	15.75 - 16.75	<2	<1	2	NA	2.87	74	37	50	NA	129
acti	WW-4D	20.5 - 21.5	1400	<2	.8	NA	11.2	280	87	88	NA	158
Re	WW-5	10 - 20	<2	0.5	<.5	.70*	<2	<2	0.8	<.5	.65*	41.8
	WW-1A	8.17 - 9.17	<2	<.5	<.5	NA	<2	<2	<.5	<.5	NA	<1
	WW-1B	11 - 12.17	<2	<.5	<.5	NA	<2	<2	<.5	<.5	NA	<1
	WW-1B-DUP		NA	NA	NA	NA	<2	NA	NA	NA	NA	<1
	WW-1C	15.67 - 16.67	<2	2	<.5	NA	<2	<2	1	<.5	NA	<1
	WW-1D	20.5 - 21.5	<2	<.5	<.5	NA	<2	12	3	<.5	NA	140
	WW-10A	7.83 - 8.83	1	0.8	1	NA	43.5	<2	<.5	<.5	NA	1.61
Down- gradient Pea Gravel	WW-10B	10.75 - 11.75	2	2	4	NA	7.78	<2	0.2	NA	NA	.73
Dov rad Pe Gra	WW-10C	15.67 - 16.5	3	5	10	NA	30.3	<2	0.9	1	NA	2.35
_ a,	WW-10D	20.67 - 21.33	4	4	5	NA	0.76	<2	1	1	NA	43
ı	WIC-9	11 - 12	800	550	830	480	927	91	70	82	60	120
nife	WIC-10	16 - 17	190	46	92	NA	95.7	5	3	8	NA	54.3
Downgradient Aquifer Wells		20.5 - 21.5	420	280	140	NA	113	46	16	7	NA	70
nt ,	WIC-11											
adient Wells	WIC-12	25 - 26	3200	3400	3400	1500	371	<200	250	360	260	63.2
gra V	PIC-31	10 - 20	NA	NA	NA	160	43.6	NA	NA	NA	17	2.39
wn	PIC-32	10 - 20	NA	NA	NA	NA	116	NA	NA	NA	NA	13
Do	PIC-32-DUP		NA	NA	NA	NA	126	NA	NA	NA	NA	13.7
	WIC-3	19 - 24 D: Not detect	1900	2900	2500	1400	1450	220	260	290	240	257

NA: Not available NI

ND: Not detected

^{*} Indicates average value taken from adjacent well (for May 2001 WW-7(A-D) values approximated with WW-11, WW-3 values approximated with WW-12, WW-5 values approximated with WW-14)

Table 3-2. Monitoring Results for Field Parameters in Groundwater

	Well ID	Screen			pН			ORP (mV)				
		Depth (ft bgs)	January 1997	April 1997	Oct. 1997	May 2001	July 2004	January 1997	April 1997	Oct. 1997	May 2001	July 2004
	WIC-1	19 – 24	6.12	NA	NA	7	NA	10	NA	NA	133.9	NA
Upgradient Aquifer Wells	WIC-5	11 - 12	4.44	7.1	7.51	NA	7.24	85	144.3	-64.7	NA	225
lier We	WIC-6	15 - 16	NA	8.8	7.63	NA	7.72	NA	92.2	10.3	NA	154
grac	WIC-7	20.5 - 21.5	5.28	7	7.17	NA	7.34	34	155.5	19.6	NA	137
Up	WIC-8	24 - 25	4.9	7.1	7.13	NA	7.34	85	157.8	18.7	NA	137
¥	WIC-8- DUP		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
1t 1	WW-7A	8.08 - 9.08	7.25	7.1	7.50	7*	7.57	7.9	101.6	14.2	229*	-44
Up- gradient Pea Gravel	WW-7B	11 - 12.17	6.91	7.1	7.24	7*	7.47	-23	122.5	20.6	229*	-123
C P	WW-7C	16 - 17	NA	7.1	7.29	7*	7.31	NA	117.1	7.3	229*	-10
	WW-7D	20.67 - 21.33	7.49	7.4	7.60	7*	7.35	-73	110.4	7.9	229*	-203
	WW-8A	8.25 - 9.42	8.74	10.2	9.42	NA	10.18	-286	-343.4	-126.5	NA	-195
	WW-8B	11.08 - 12.08	9.39	10.2	10.03	NA	10.29	-294	-327.5	-134.4	NA	-222
	WW-8C	15.92 - 16.75	NA 10.44	9.9	10.03	NA	10.09	NA 264	-309	-149.6	NA	-221
	WW-8D	20.5 - 21.5	10.44	11.2	11.72	NA 10.0*	10.36	-364	-359.3	-125.4	NA -40.2*	-252
	WW-3 WW-4A	10.5 - 20.5 7 - 8	9.47 8.46	10.4 10.5	10.14 10.01	10.0*	10.20 10.65	-305 -316	-359 -496	-112 -47.8		-262 -397
slls	WW-4A WW-4B	10 - 11	8.86	10.5	9.54	NA NA	10.65	-273	-602.9	-47.8 -76.6	NA NA	-368
×	WW-4C	15.75 - 16.75	8.3	10.3	9.97	NA NA	10.84	-273	-405.2	-76.6	NA NA	-213
Reactive Wells	WW-4D	20.5 - 21.5	8.47	10.1	10.43	NA NA	9.85	-322	-403.2	-111.4	NA NA	-215
act	WW-5	10 - 20	8.59	10.6	10.99	10.9*	10.82	-309	-655.9	90	-820.8*	-264
Re	WW-1A	8.17 - 9.17	9.08	10.4	11.82	NA	10.62	-353	-529.2	-250.8	NA	-418
	WW-1B	11 - 12.17	9.94	10.5	9.61	NA	10.84	-459	-477.9	-147.2	NA	-422
	WW-1B- DUP		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	WW-1C	15.67 - 16.67	9.72	10.5	9.01	NA	11.16	-379	-638.9	-162.8	NA	-392
	WW-1D	20.5 - 21.5	10.03	10.9	9.38	NA	11.03	-445	-610.6	-104.4	NA	-278
. +	WW-10A	7.83 - 8.83	9	9.9	10.36	NA	10.23	0.0	-554.6	-105.8	NA	-322
Down- gradient Pea Gravel	WW-10B	10.75 - 11.75	7.77	9	9.06	NA	10.51	-285	-433.8	-34.8	NA	-292
Ped Gra	WW-10C	15.67 - 16.5	7.27	9	9.35	NA	9.82	-10	-351.9	-123.8	NA	-245
_ 00 _	WW-10D	20.67 - 21.33	7.39	10.5	10.23	NA	10.67	-260	-364.6	-131.8	NA	-257
	WIC-9	11 - 12	7	7.1	7.23	7.3	7.61	10	-16.4	49.3	NA	-29
Downgradient Aquifer Wells	WIC-10	16 - 17	8.09	8.4	8.40	NA	9.37	110	-149.7	39.4	NA	-90
	WIC-11	20.5 - 21.5	7	12	12.05	NA	11.12	0.0	-245	8.61	141.1	-204
	WIC-12	25 - 26	7.14	7	7.40	7.0	7.25	-3	9.6	43.5	NA	57
die Vel	PIC-31	10 - 20	NA	NA	NA	9.3	10.03	NA	NA	NA	NA	-71
gra V	PIC-32	10 - 20	NA	NA	NA	NA	10.90	NA	NA	NA	-13.2	-188
Down	PIC-32- DUP		NA	NA	NA	NA	NA	NA	62.1	NA	-137.3	NA
	WIC-3	19 - 24	6.97	6.9	7.11	7.0	6.95	34	NA	84.2	121.9	49
	NA: Not ava	oileble										

NA: Not available.

ND: Not detected.

^{*} Indicates average value taken from adjacent well (for May 2001 WW-7(A-D) values approximated with WW-11, WW-3 values approximated with WW-12, WW-5 values approximated with WW-14)

Table 3-3. Key Cations in Groundwater

			Ca (mg/L) Mg (mg/L)									
	Well ID	Screen Depth (ft bgs)	January 1997	April 1997	Oct. 1997	May 2001	July 2004	January 1997	April 1997	Oct. 1997	May 2001	July 2004
	WIC-1	19 - 24	165	158	NA	180	NA	63.7	58.3	NA	65	NA
nt :IIs	WIC-5	11 - 12	134	137	95.3	NA	87.5	45.6	49.9	38.7	NA	35.1
lier	WIC-6	15 - 16	136	134	149	NA	120	62.8	63.6	56.5	NA	44.2
Upgradient Aquifer Wells	WIC-7	20.5 - 21.5	159	159	173	NA	160	60.7	61.2	63.6	NA	64.5
Up	WIC-8	24 - 25	158	158	167	NA	155	60.8	59.3	61	NA	61.6
A	WIC-8- DUP		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
ıt 1	WW-7A	8.08 - 9.08	152	164	NA	170*	106	63.5	65.7	NA	66*	50.9
Up- gradient Pea Gravel	WW-7B	11 - 12.17	159	163	NA	170*	140	63.5	63.7	NA	66*	61.6
Cr. P. Cr.	WW-7C	16 - 17	157	177	153	170*	159	63.1	72.8	61	66*	63
	WW-7D	20.67 - 21.33	6.96	164	175	170*	160	49.9	63.9	64.8	66*	65.9
	WW-8A	8.25 - 9.42	17.5	2.02	NA	NA	1.4	58.8	30.4	NA	NA	4.3
	WW-8B	11.08 - 12.08	8.8	2.25	NA	NA	1.3	57.3	17.5	NA	NA	11.5
	WW-8C	15.92 - 16.75	5.36	3.49	NA	NA	1.2	52.8	32.8	NA	NA	18.6
	WW-8D	20.5 - 21.5	16.2	8.27	NA 2.55	NA 1.2*	3.0	29.4	16.3	NA 4.25	NA 14*	11.8
	WW-3 WW-4A	10.5 - 20.5 7 - 8	5.45	2.41	2.55 NA	1.3*	1.5 .5	52.4 44.2	10.1	4.35	14*	15.8 .53
Reactive Wells	WW-4A WW-4B	10 - 11	18.4 10.1	3.51 5.4	NA NA	NA NA	1.9	44.2	2.88	NA NA	NA NA	1.01
×	WW-4B WW-4C	15.75 - 16.75	4.06	2.39	2.29	NA NA	1.9	43.2	28.9	9.86	NA NA	12.6
ive	WW-4D	20.5 - 21.5	154	2.71	2.76	NA	1.9	61.3	42.3	16.1	NA	44.3
act	WW-5	10 - 20	8.59	3.22	2.73	1.0*	1.2	26.4	.896	.362	<0.5	8.03
Re	WW-1A	8.17 - 9.17	29.8	1.96	NA	NA	.4	46.9	.68	NA	NA	<.1
	WW-1B	11 - 12.17	50.6	6.47	NA	NA	.7	25.1	1.07	NA	NA	<.1
	WW- 1B-DUP		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	WW-1C	15.67 - 16.67	8.29	.891	.893	NA	1.8	40.2	1.15	.413	NA	<.1
	WW-1D	20.5 - 21.5	34.4	29.6	6	NA	39.7	.188	.159	.131	NA	6.78
	WW- 10A	7.83 - 8.83	54.7	1.41	NA	NA	NA	30.4	.593	NA	NA	NA
Down- gradient Pea Gravel	WW- 10B	10.75 - 11.75	52.3	5.21	NA	NA	NA	10.3	1.13	NA	NA	NA
Doy grac P	WW- 10C	15.67 - 16.5	52.6	7.51	7.03	NA	NA	10.9	2.31	1.37	NA	NA
	WW- 10D	20.67 - 21.33	52.5	13.2	8.86	NA	NA	12.3	.327	.315	NA	NA
	WIC-9	11 - 12	72.6	58	41.8	26	19.4	24	20.9	14	8.3	5.95
Aquifer	WIC-10	16 - 17	55.8	12.7	10.6	NA	9.5	6.82	1.52	1.18	NA	.12
	WIC-11	20.5 - 21.5	111	ND	102	NA	18.7	.019	ND	.025	NA	<.1
snt ,	WIC-12	25 - 26	125	132	131	180	123	42.1	44.1	43.4	65	41.9
adie We.	PIC-31	10 - 20	NA	NA	NA	14	NA	NA	NA	NA	NA	NA
ngra,	PIC-32	10 - 20	NA	NA NA	NA	NA	NA	NA NA	NA NA	NA NA	NA NA	NA NA
Downgradient / Wells	PIC-32- DUP	10. 24	NA	NA	NA 170	NA 100	NA	NA 50.2	NA	NA	NA	NA
	WIC-3	19 - 24	159	162	179	190	NA	59.3	57.9	63.2	65	NA
N	IA: Not av	railable										

NA: Not available

ND: Not detected

^{*} Indicates average value taken from adjacent well (for May 2001 WW-7(A-D) values approximated with WW-11, WW-3 values approximated with WW-12, WW-5 values approximated with WW-14

Table 3-4. Key Anions in Groundwater

No. Depth (ft bgs) 1997 1997 1997 2001 2004 1997 1997 1997 2001 2001 2005				SO ₄ (mg/L) Alkalinity (mg/L)						L)			
Wic-5			Depth							April 1997			July 2004
DUP		WIC-1	19 - 24	346	349	NA	360	NA	377	314	NA	390	NA
DUP	at SIIs	WIC-5	11 - 12	442	322	214	NA	188	267	250	260	NA	216
DUP	dier	WIC-6	15 - 16	335	352	355	NA	230	336	288	376	NA	213
DUP	grae	WIC-7	20.5 - 21.5	247	350	330	NA	281	378	330	378	NA	411
DUP	Up		24 - 25	318	362	358	NA	287	346	273	378	NA	403
No. No.	A	DUP				NA					NA		NA
WW-BA 8.25 - 9.42 249 56.7 NA NA <3 54.4 <1000 NA NA 65.5 NA NA <3 54.4 <1000 NA NA <10 NA NA NA <10 NA NA NA <10 NA NA NA NA NA NA NA N	ıt 1												282
WW-BA 8.25 - 9.42 249 56.7 NA NA <3 54.4 <1000 NA NA 65.5 NA NA <3 54.4 <1000 NA NA <10 NA NA NA <10 NA NA NA <10 NA NA NA NA NA NA NA N	p- dier ea ave												386
WW-BA 8.25 - 9.42 249 56.7 NA NA <3 54.4 <1000 NA NA 65.5 NA NA <3 54.4 <1000 NA NA <10 NA NA NA <10 NA NA NA <10 NA NA NA NA NA NA NA N	D grac												408
WW-8B	5.5						_						
WW-8C 15.92 - 16.75 170 94.4 NA NA 8.42 82.2 70.8 NA NA NA 123													65.3
WW-8D 20.5 - 21.5 154 51 NA NA 48.8 50.3 62.2 NA NA 88.8													
WW-3													_
WW-4A													
WW-4B												-	
WW-1A 6.17-9.17 271 3.2 NA NA S3 97.7 14.7 NA NA 22 14.7 NA NA 22 14.7 NA NA NA NA NA NA NA N	sills					1							
WW-1A 6.17-9.17 271 3.2 NA NA S3 97.7 14.7 NA NA 22 14.7 NA NA 22 14.7 NA NA NA NA NA NA NA N	š												
WW-1A S.17-9.17 271 3.2 NA NA S.3 97.7 14.7 NA NA 22 NA NA NA NA NA	.i.e					1							
WW-1A 6.17-9.17 271 3.2 NA NA S3 97.7 14.7 NA NA 22 14.7 NA NA 22 14.7 NA NA NA NA NA NA NA N	act					1							
WW-1B	Re					1							
WW-1B-DUP WW-1C 15.67 - 16.67 191 7.4 9.3 NA 3 <10 15.3 26.9 NA 55.3 WW-1D 20.5 - 21.5 77.5 54.7 1.3 NA 113 241 40.3 55 NA 53.4 WW-1D 20.5 - 11.75 177 4.6 NA NA NA <10 12.4 NA NA NA NA NA WW-1D 15.67 - 16.5 214 11 5.2 NA NA <10 13.6 31.6 NA NA NA WW-1DD 20.67 - 21.33 222 29 6.5 NA NA <10 19.4 34.9 NA NA WIC-9 11 - 12 183 121 70.1 81 31.7 172 <1000 117 140 69.6 WIC-10 16 - 17 203 19 13.2 NA 38.1 12.7 18.3 42.7 NA 73.5													29.1
WW-1D 20.5 - 21.5 77.5 54.7 1.3 NA 113 241 40.3 55 NA 53.4					NA	NA	NA		NA	NA	NA		NA
WW-10A 7.83 - 8.83 282 1 NA NA <10 12.4 NA					7.4	9.3	NA	<3					55.5
WW-10B 10.75 - 11.75 177 4.6 NA NA <10 <10 NA		WW-1D	20.5 - 21.5	77.5	54.7	1.3	NA	113	241	40.3	55	NA	53.4
WIC-10 16-17 203 19 13.2 NA 38.1 12.7 18.3 42.7 NA 75.4	ıt .												NA
WIC-10 16-17 203 19 13.2 NA 38.1 12.7 18.3 42.7 NA 75.4	wn- tien ea tvel												NA
WIC-10 16-17 203 19 13.2 NA 38.1 12.7 18.3 42.7 NA 75.4	Do P. P. Gre												NA
WIC-10 16-17 203 19 13.2 NA 38.1 12.7 18.3 42.7 NA 75.4	5.5												NA
WIC-10 16 - 17 203 19 13.2 NA 38.1 12.7 18.3 42.7 NA 75.2													69.6
VIC-11 20.5 - 21.5 125 ND 20 NA 74.5 609 ND 363 NA 106	nt Aquifer lls	WIC-10				1							75.5
물을 PIC-31 10-20 NA NA NA NA NA NA NA 62											308		267
	ldie Wel												
PIC-32 10 - 20 NA	igra 1		10 - 20			1							NA
PIC-32- DUP NA N	Down						·						NA
WIC-3 19 - 24 344 347 296 390 NA 362 NA NA NA NA NA NA			-	344	347	296	390	NA	362	NA	NA	NA	NA

NA: Not available ND: Not detected

^{*} Indicates average value taken from adjacent well (for May 2001 WW-7(A-D) values approximated with WW-11, WW-3 values approximated with WW-12, WW-5 values approximated with WW-14

3.1 Trends in TCE

As seen in Table 3-2, TCE concentrations in the upgradient aquifer (WIC-5 to -8) and pea gravel (WW-7A, B, C, and D) have fluctuated around 1,000 ppb since 1996 (see also Figure 3-1). Along the flow path into the reactive cell, TCE concentrations drop considerably to below MCL (5 ppb) in the first well cluster WW-8, very near the upgradient edge of the iron. The sharp drop in TCE concentration barely 0.5 ft along the flow path is interesting because it seems to indicate that groundwater flow must be extremely slow through the iron (residence time must be high). Occasionally elevated TCE levels in wells WW-3 and WW-4D indicate that there are preferential pathways through the iron that may lead to lower residence times for some parts of the PRB. In the well cluster (WW-1) closest to the downgradient edge of the iron, TCE levels were consistently below detection, thus indicating that the design thickness of the PRB has been sufficient to treat TCE to target levels. It is important that the water exiting the reactive cell, as indicated by the TCE concentrations in well cluster WW-1, be below target cleanup level (5 ppb) because the well or well cluster closest to the downgradient edge in the iron is often considered a temporary compliance point, until the downgradient aquifer starts showing an improvement in contaminant levels.

Further downgradient, in the pea gravel, in wells WW-10A, B, and C, TCE concentrations appear to rebound to as high as 43.5 ppb. Because TCE levels in the nearest reactive cell cluster WW-1 appear to be below detection, elevated TCE levels in the downgradient pea gravel possibly indicate diffusion from historical TCE present in the downgradient aquifer. In the shallower depths (A and B depths in the well clusters), where groundwater flow is slow, diffusion may play a relatively bigger role in determining TCE levels in the downgradient pea gravel. Downgradient aquifer well WIC-9 (screened at a depth corresponding to the B wells) has shown persistently high levels of TCE (927 ppb during the July 2004 round). This shallow portion of the downgradient aquifer does not appear to have encountered much flushing with treated water emerging from the PRB because of the slow flow at this depth.

On the other hand, deeper wells WIC-11 and WIC-12 in the downgradient aquifer have shown progressively lower TCE levels in the last two rounds. TCE levels in WIC-11 have progressively declined from approximately 400 ppb in 1997 to approximately 100 ppb in 2004. TCE levels in WIC-12 have progressively declined from approximately 3,000 ppb in 1997 to under 400 ppb in 2004. There is more evidence of flushing of the downgradient aquifer with treated water emerging from the PRB at these depths.

3.2 Trends in DCE

As seen in Table 3-1, DCE, which has a slower reaction rate with the ZVI (higher half life), shows a somewhat different trend along the flow path through the PRB. DCE concentrations of approximately 200 ppb in the upgradient aquifer and pea gravel decline as the groundwater enters the reactive cell. However, compared to TCE, DCE takes longer to decline to below MCL (70 ppb). At all depths in well cluster WW-8, DCE levels are above 70 ppb. Elevated levels of DCE persist through cluster WW-4, especially at the b, C, and D depths. At the A-depth in both clusters (WW-8 and WW-4), there is more of a decline in DCE, probably because of the slower moving groundwater (higher residence time). At the deepest layer within the PRB (D wells in each cluster), DCE concentration remained relatively high, especially in the July 2004 event. At WW-1D, the groundwater exiting the reactive cell showed a DCE concentration of 140 ppb in July 2004. The persistence of DCE through the reactive cell during this monitoring round may indicate both a preferential flow path to this well through the ZVI, as well as possibly some deterioration in the reactivity of the ZVI that has been exposed to a greater mass flux of dissolved solids (greater depletion of surface reactive sites) due to higher groundwater flow during the last 8 years. The oxidation-reduction potential (ORP) measurements discussed below provide some support to this hypothesis.

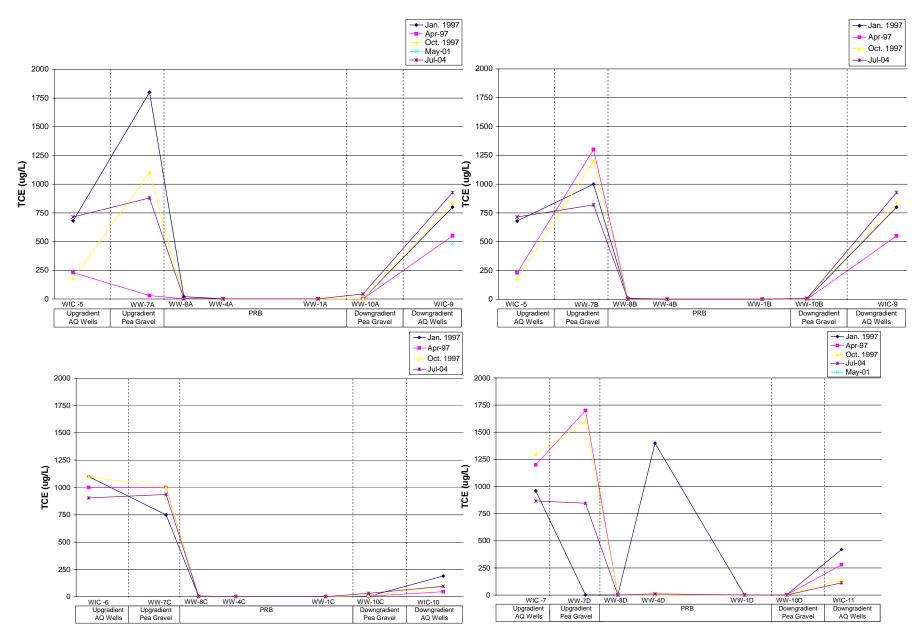


Figure 3-1. Spatial and Temporal Trends in TCE in Shallow (A and B) and Deep (C and D) Wells

Figure 3-2 illustrates the differences in DCE degradation profiles at various depths in the PRB. The DCE has to travel progressively further along the flow direction in the ZVI to reach non-detect levels, as we go from shallower to deeper layers. Elevated DCE levels persist to some degree in the wells in the downgradient pea gravel and aquifer. One other possible factor driving these TCE and DCE trends may be microbial growth (Roberts et. al. 1996). Abiotic reduction of TCE through predominantly beta-elimination pathway leads to ethene formation, whereas microbially-driven anaerobic reductive dechlorination proceeds primarily along the hydrogenolysis pathway leading to formation of DCE and vinyl chloride. Although previous research has indicated the unlikelihood of microbial growth deep inside the iron (Gavaskar et al. 1998), where pH levels are unsuitably high, microbial communities could potentially thrive in regions where ORP levels are moderately low and pH levels are moderately high (e.g., near the upgradient edge of the iron and in the downgradient aquifer). Mildly reducing (anaerobic) and moderate pH conditions could eventually result in the ZVI itself, as surface reactive sites are used up by exposure to groundwater flow.

3.3 Trends in ORP and pH

The spatial trends in ORP and pH are as expected (see Table 3-2 and Figure 3-3). Zerovalent iron, a strong reducing agent creates strongly reducing conditions in the reactive cell. ORP becomes progressively lower along the flow path through the reactive cell, as the contact time with the iron increases. Although measurements have fluctuated among events, ORP levels as low as -820 mV have been measured inside the iron, indicating that strongly reducing conditions necessary to initiate abiotic reactions have been generated. However, in July 2004, the lowest ORP level measured in the reactive cell was -422 mV. In general, across the iron, ORP levels appear to have risen in July 2004. This may indicate that the reactivity of the iron, although still quite strong, is not as strong now after 8 years of operation, as it was in the past when the iron was newer. One consequence of this slight aging of the iron is that, as noted above, the PRB may not be removing the less oxidized CVOCs, such as DCE, as efficiently as it has in the past. Also, as mentioned above, faster flow in the deepest layer in the reactive cell could be responsible for lower residence time and, therefore, higher ORP measured in the reactive cell exit well WW-10D.

On the other hand pH levels in the iron have generally remained relatively stable or have increased slightly over time, peaking at 11.16 in WW-1C in July 2004. Hydroxyl radicals are produced when iron breaks down water under strong reducing conditions and this causes an increase in pH. The pH is does not appear to be as impacted over time as is ORP. This divergence between ORP and pH in aging PRBs has been noticed before at other sites, such as Elizabeth City (Wilkin and Puls, 2003). ORP appears to be a more sensitive indicator of the aging of iron than pH and ORP changes tend to be more evident earlier on. As the water emerges from the iron into the downgradient pea gravel, ORP and pH persisted at levels similar to those in the iron, especially in the later sampling events. The type of rebound seen in TCE and DCE concentrations as the water enters the downgradient pea gravel is not evident with these native parameters. One possibility is that some intermixing of the iron particles and pea gravel has occurred over time and some iron particles have migrated into the pea gravel, thus creating more reducing conditions there. This may be true even in the upgradient pea gravel, where the ORP has declined substantially over time, although pH continues to be similar to that of the aquifer. Another factor may be that the water exiting the reactive cell is retaining some of its reduced state. As the water exits the downgradient pea gravel and enters the aquifer, ORP continued to be relatively low and pH continued to be relatively high in WIC-9 and WIC-10 wells. In fact ORP and pH are two strong indicators that support the observation that a treated groundwater front is emerging from the PRB and that the downgradient water quality is improving. Implicit in these observations is the reassurance, after many years of operation, that flow through the PRB is occurring and that a gradual improvement in downgradient water quality compliance is probable.

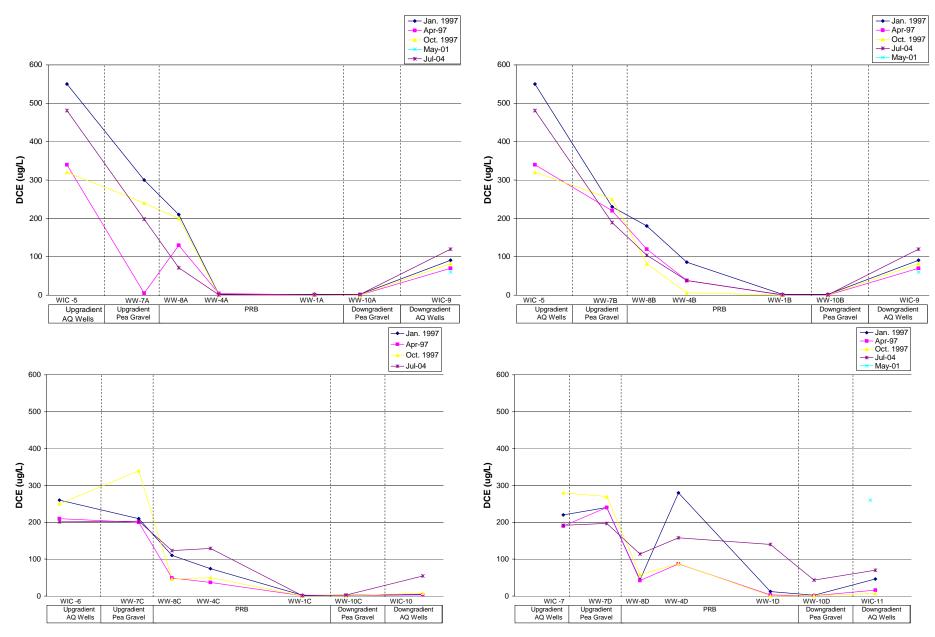


Figure 3-2. Spatial and Temporal Trends in DCE in Shallow (A and B) and Deep (C and D) Wells

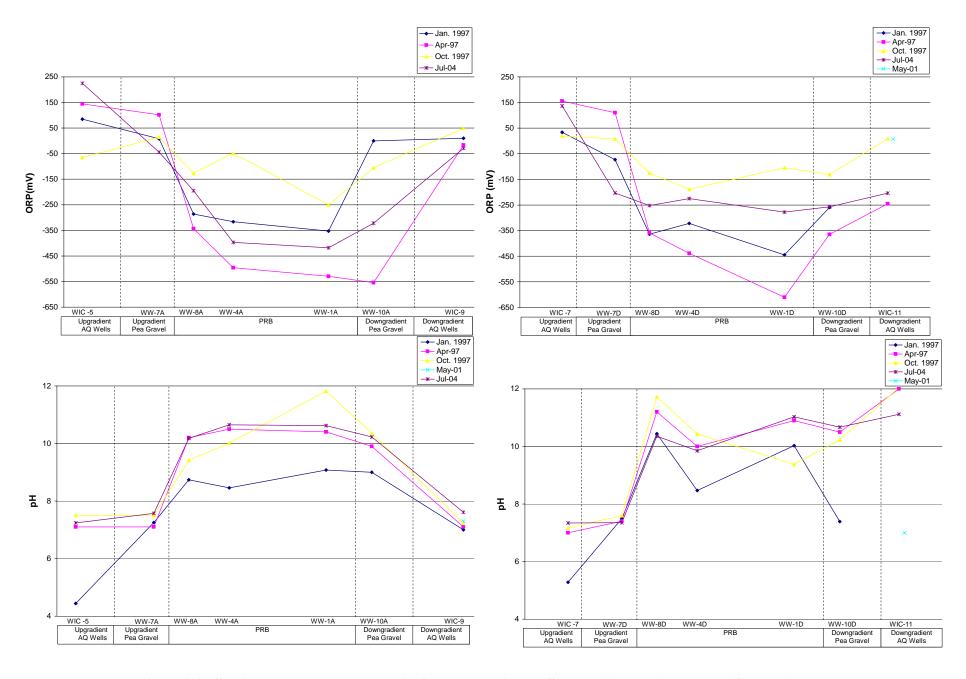


Figure 3-3. Spatial and Temporal Trends in ORP and pH in and Shallow (A and B) and Deep (C and D) Wells

The degree of rebound in ORP and pH levels in the downgradient aquifer wells is another indicator of the layered flow at this site. In the shallower wells, where flow is much slower, the ORP and pH reflect conditions closer to those in the surrounding aquifer. In the deeper wells, ORP and pH are closer to their levels in the reactive cell. On the other hand, the ORP and pH rebound has been greatest in the deepest downgradient aquifer well WIC-12, where water exiting the PRB is probably mixing with groundwater flowing under the PRB, through the gap between the PRB and the thin aquitard.

3.4 Trends in Native Geochemical Constituents

Calcium, magnesium, sulfate, and alkalinity (carbonate) are all native constituents of the groundwater that are likely to react in the iron cell. Under the high-pH conditions prevalent in the iron, calcium and magnesium can precipitate out as carbonates. Under the low-ORP conditions, assisted by microbial action, sulfate can be reduced to sulfide. All these trends are evident at this site.

As seen in Table 3-3, Calcium levels fell from a maximum of 160 mg/L in the upgradient aquifer to below 1 mg/L in some wells inside the reactive cell in July 2004 (Figure 3-4). Magnesium levels fell from a maximum of 64.5 mg/L in the upgradient aquifer to below 0.1 mg/L in some wells inside the reactive cell in July 2004. Sulfate levels declined from a maximum of 287 mg/L in the upgradient aquifer to below 3 mg/L (Figure 3-5). Alkalinity levels declined from a maximum of 411 mg/L in the upgradient aquifer to a low of 12.5 mg/L inside the reactive cell in 2004. Calcium and magnesium carbonates, iron carbonates, and iron sulfide are some of the precipitates commonly found depositing on iron surfaces at Moffett Field and other sites (Gavaskar et. al. 2002). This precipitation is likely to reduce the reactivity of the iron, as it ages, by blocking electron transfers from the iron to the bulk of the water. This results in a gradual rebound in ORP levels and eventually in a deterioration of CVOC degradation rates, as has been observed in the most recent sampling event at Moffett Field.

The inorganics data in Table 3-3 are yet another indicator that the ZVI in the deeper portion of the aquifer may be aging faster because of the faster flow in this region. For example, in July 2004, the calcium level rebounded to 39.7 mg/L in the reactive cell exit well (WW-1D) and so also did the levels of magnesium (to 6.78 mg/L in WW-1D) and sulfate (to 113 mg/L in WW-1D), compared to previous sampling events. In previous rounds, WW-1D had showed a sharper decline in the levels of these parameters.

Because sulfate reduction rates are tied to microbial activity, progressively lower sulfate concentrations over time near the upgradient end of the iron (WW-8 cluster) indicate that the population of sulfate-reducing bacteria may have grown over the years, in the strongly reducing, but pH-benign, environment near the front end of the iron (see Table 3-4). Further along the flow path in the iron, as pH increases, the environment becomes more hostile to microbial growth. Any sulfate that has not yet been reduced by the time it reaches the high-pH environment probably persists in the water as it exits the iron on the downgradient side. This could be the reason why somewhat elevated sulfate levels persist in the deeper wells (WW-8D, WW-4D, and WW-1D), where the water is probably flowing faster and gets insufficient contact time with the reactive medium and microbial populations. Figure 3-5 illustrates the increase in sulfate reduction efficiency from January 1997 soon after the PRB was first built to July 2004, 8 years later; this is probably the consequence of a general growth in sulfate reducing populations near the upgradient end of the iron.

As with other groundwater parameters, such as ORP and pH, the decrease in calcium, magnesium, sulfate, and alkalinity levels induced in the PRB persists to some extent in the downgradient pea gravel and aquifer. The rebound of these parameters to upgradient aquifer levels is sharpest in the deepest well WIC-12, where treated water exiting the PRB mixes with untreated groundwater flowing under the PRB.

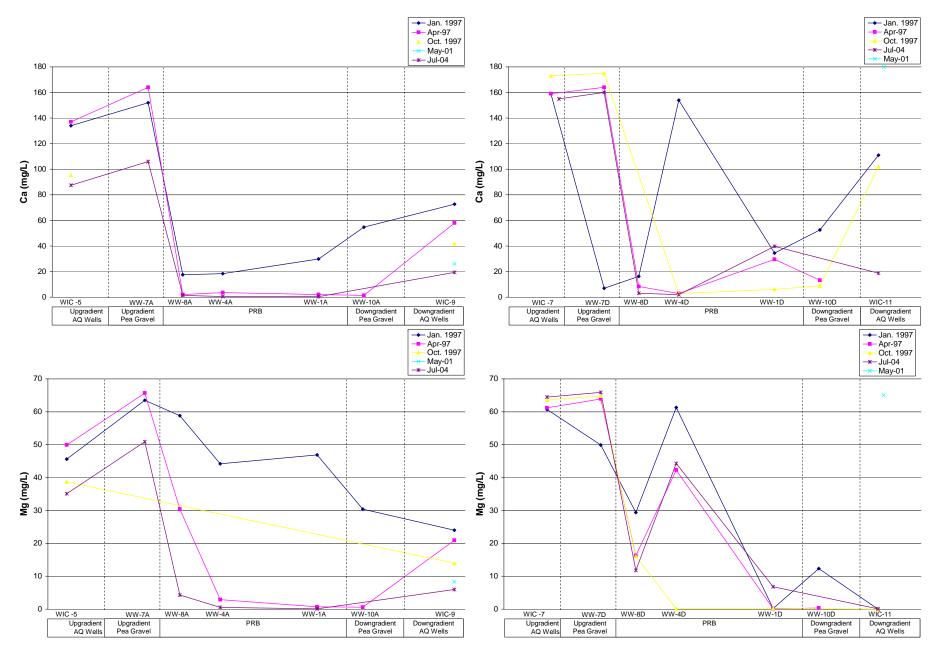


Figure 3-4. Spatial and Temporal Trends in Ca and Mg in and Shallow (A and B) and Deep (C and D) Wells

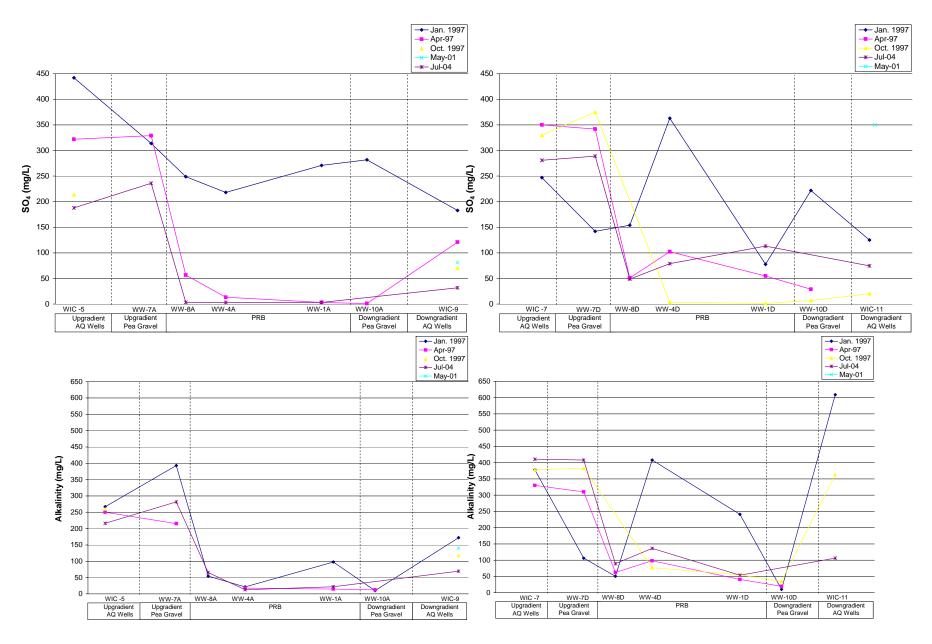


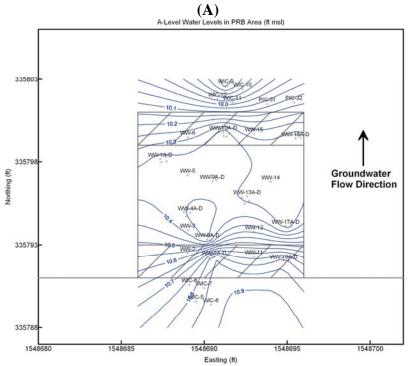
Figure 3-5. Spatial and Temporal Trends in SO₄ and Alkalinity in and Shallow (A and B) and Deep (C and D) Wells

3.5 Hydrogeologic Trends

Figures 3-6 and 3-7 show the maps of water level measurements collected in the A, B, C, and D level wells (corresponding approximately to geologic Layers 1, 2, 3, and 4 respectively). These maps are fairly similar, but the hydraulic gradient in the deeper layers (Layers 3 and 4 or Wells B, C, and D) is a bit sharper, especially near the transitions between the downgradient pea gravel and aquifer and between the upgradient pea gravel and iron. At both these interfaces, water has a tendency to mound a bit before moving from a higher-permeability medium to a lower-permeability medium. This is evident from the sharper gradients seen at the interface between the upgradient pea gravel and reactive cell and at the interface between the downgradient pea gravel and downgradient aquifer. In general, the water level maps appear to agree with the water chemistry findings, which indicate that water may be moving faster in the deeper layers than in the shallower layers of the PRB.

The best indicators of hydrogeologic trends in and around the PRP are the trends in the groundwater chemistry that were discussed above and that provide insights into the residence times (reaction times) encountered by the groundwater as it flows through the PRB. Because the PRB is a very high-permeability, high-porosity environment compared to the aquifer, hydraulic gradients that are already relatively low in the aquifer become even lower inside the PRB. Water level measurements inside a PRB often show very little change with distance. Therefore, flow conditions inside the PRB may be better deduced indirectly from the trends in water chemistry, as the authors have attempted to do in the sections above. However, a careful analysis of water level measurements and groundwater modeling conducted at this site does confirm some of the trends observed in the water chemistry data.

One recent modeling study (Thomson and Vidumsky, 2004) has indicated the possibility that vertical (downward) flows occurs when groundwater enters the higher-permeability environment in the PRB, leading to somewhat stagnant zones in the shallower portions of the PRB and downgradient aquifer and stronger flow in the deeper portions of the PRB. This vertical flow phenomenon was not evident in the water level data at Moffett Field. Vertical water level differences in wells within the same cluster are not significant enough to indicate strong vertical flows in this PRB (see Table 3-5). On the other hand, vertical stratification of flow (slower flow in shallow regions and faster flow in deeper regions) within the PRB is evident in the groundwater chemistry data, more so than in the water level measurements, and appears to be related more to the flow stratification inherent in the hydrogeology of the aquifer than in any new vertical flow patterns within the reactive cell.



*note: water levels within multilevel wells (A,B,C, and D screens) were within 0.012 m of each other.

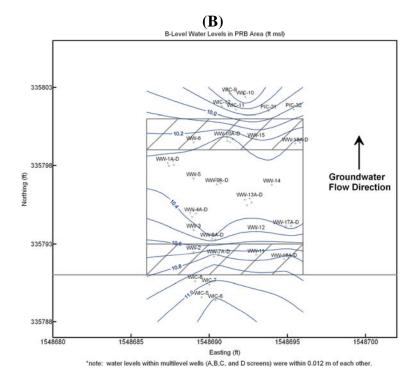
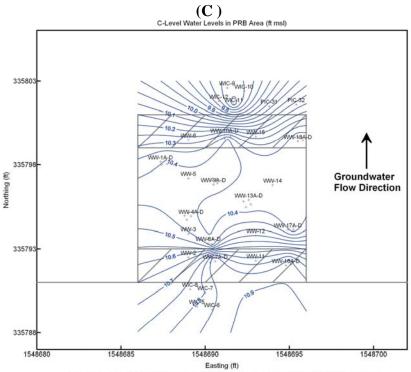


Figure 3-6. Water Level Maps for A and B Level Wells



*note: water levels within multilevel wells (A,B,C, and D screens) were within 0.012 m of each other.

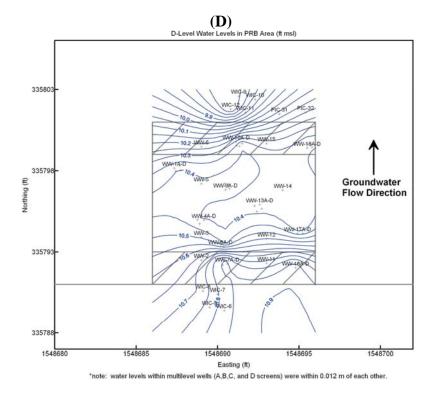


Figure 3-7. Water Level Maps for C and D Level Wells

Table 3-5. Vertical Gradients in the PRB

Well Id	Easing	Northing	Location/ Aquifer	Water Level (ft msl) 7/26/2004	Vertical Gradient* (ft)
WW-7A	1548690.59	335792.26		10.85	
WW-7B	1548690.29	335792.18	Upgradient	10.85	0.02 ↓
WW-7C	1548690.56	335792.46	Pea Gravel	10.84]
WW-8D	1548690.31	335792.51		10.83	
WW-16A	1548694.79	335792.02		10.83	
WW-16B	1548695.09	335792.09	Upgradient	10.84	0.01↓
WW-16C	1548694.98	335792.33	Pea Gravel	10.81	
WW-16D	1548694.73	335792.25		10.82	
WW-8A	1548690.18	335793.33		10.34	
WW-8B	1548690.17	335793.63	Reactive	10.36	0.03↑
WW-8C	1548690.37	335793.29	Cell	10.36	
WW-8D	1548690.44	335793.60		10.37	1
WW-17A	1548694.91	335794.13		10.32	
WW-17B	1548695.24	335794.35	Reactive	10.32	0.02↓
WW-17C	1548695.23	335794.14	Cell	10.32	1
WW-17D	1548695.04	335794.51		10.30	
WW-4A	1548689.16	335794.94		10.34	
WW-4B	1548688.77	335794.97	Reactive	10.37	0.01↑
WW-4C	1548688.90	335794.72	Cell	10.37	1
WW-4D	1548689.98	335795.11	1	10.35	1
WW-13A	1548692.58	335795.91		10.34	
WW-13A	1548692.70	335795.65	Reactive	10.33	0.01↓
WW-13A	1548692.41	335795.48	Cell	10.33	1
WW-13A	1548692.27	335795.82		10.33	1
WW-9A	1548690.48	335796.83		10.38	
WW-9B	1548690.66	335796.16	Reactive	10.37	0.01↓
WW-9C	1548690.72	335796.91	Cell	10.36	1
WW-9D	1548690.42	335796.20		10.37	
WW-1A	1548687.34	335798.17		10.37	
WW-1B	1548687.41	335797.98	Reactive	10.35	0.01↓
WW-1C	1548687.67	335798.31	Cell	10.35	
WW-1D	1548687.73	335798.04]	10.36	
WW-10A	1548691.14	335799.80		10.38	
WW-10B	1548691.16	335799.58	Downgradient	10.37	0.04↓
WW-10C	1548691.33	335799.51	Pea Gravel	10.36	1
WW-10D	1548691.50	335799.70	1 1	10.34	1
WW-18A	1548695.50	335799.41		10.34	
WW-18A	1548695.80	335799.46	Downgradient	10.34	0.01↑
WW-18A	1548695.53	335799.66	Pea Gravel	10.34	1
WW-18A	1548695.74	335799.65	1	10.35	1

Section 4.0: CONCLUSIONS

The PRB at Moffett Field continues to substantially degrade target CVOCs after 8 years of operation. There also are no signs that the hydraulic performance of the PRB (groundwater capture and residence time) has been noticeably affected over this time period. Many economic calculations have indicated that as long as the ZVI retains sufficient reactive and hydraulic performance for at least 10 years, the present value (PV) of its investment is less than that of a comparable pump-and-treat system (Gavaskar et al., 2002). Therefore, confirmation of this PRB's long-term performance is important for this and other similar PRBs that have been applied at dozens of sites for long-term groundwater treatment. Also important is the finding that for the first time at this site, the downgradient groundwater quality is showing signs of improvement, as more of the treated water, especially in the deeper portions of the aquifer, flushes the pre-existing contamination in the downgradient soils (the PRB was installed in the middle of the plume, so a part of the original plume still exists downgradient of the PRB). This finding eases the regulatory compliance concerns in the downgradient aquifer, where pre-existing CVOC contamination has persisted for several years after installation of the PRB.

Other important findings are that flow through the PRB is not uniform, partly because the ZVI itself is probably not uniformly packed in the reactive cell and partly because the heterogeneities of the flow in the layered aquifer are being retained as the groundwater flows inside the PRB. These disparities in the flow have probably translated into disparities in the aging of the ZVI. In the deeper portions of the PRB, where groundwater flow is greater (and the mass flux of potentially passivating, dissolved inorganic constituents is high), the ZVI appears to have aged more than in the shallower regions. The aging of the deeper ZVI has not noticeably affected TCE degradation efficiency yet, but DCE, which reacts more slowly with the ZVI, appears to be persisting at increasing levels in the groundwater, as it exits the reactive cell. The increasing levels of dissolved calcium, magnesium, carbonates, and sulfate in the groundwater exiting the deeper portions of the reactive cell also indicate some decline in the reactivity of the deeper ZVI. Groundwater pH does not yet reflect the increasing passivation of the deeper ZVI, but ORP shows some signs of rebounding in the deeper wells along the downgradient edge of the reactive cell.

Section 5.0: REFERENCES

- Gavaskar, A., B. Sass, N. Gupta, E. Drescher, W. Yoon, J. Sminchak, J. Hicks, and W. Condit. 2002. Evaluating the Longevity and Hydraulic Performance of Permeable Barriers at Department of Defense Sites. Final report prepared by Battelle, Columbus, Ohio for Naval Facilities Engineering Service Center, Port Hueneme, CA. April 24. Project funded by ESTCP.
- Gavaskar, A., B. Sass, N. Gupta, J. Hicks, S. Yoon, T. Fox, and J. Sminchak. 1998. *Performance Evaluation of a Pilot-Scale Permeable Reactive Barrier at Former Naval Air Station Moffett Field, Mountain View, California*. Final report prepared by Battelle, Columbus, Ohio for Naval Facilities Engineering Service Center, Port Hueneme, CA. Project Sponsored by ESTCP.
- Liang, L., N. Korte, B. Gu, R. Puls, and C. Reeter. Geochemical and microbial reactions affecting the long-term performance of in situ "iron barriers." *Advances in Environmental Research*, 2000, 4, 273-286.
- Roberts, A.L., L.A. Totten, W.A.Arnold, D.R.Burris, and T.J.Campbell. 1996. "Reductive Elimination of Chlorinated Ethylenes by Zero-Valent Metals." *Environmental Science and Technology*. 30(4):2654-2659
- Thomson, M. and J. Vidumsky. Vertical flow within permeable reactive barriers: fact or fiction? 2004. In *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, May 24-27, Monterey, CA. Battelle Press, Columbus, Ohio.
- Wilkin, R. and R. Puls. 2003. Capstone Report on the Application, Monitoring, and Performance of Permeable Reactive Barriers for Groundwater Remediation: Volume 1 Performance Evaluation at Two Sites. August. EPA/600/R-03/045a.

